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Tunable Dipolar Magnetism in High-Spin Molecular Clusters

M. Evangelisti,[1,*] A. Candini,[1,2] A. Ghirri,[1,2] M. Affronte,[1,2] G. W. Powell,[3] I. A. Gass,[4] P. A. Wood,[4] S. Parsons,[4] E. K. Brechin,[4] D. Collison,[3] and S. L. Heath[3]

[1]*National Research Center on "nanoStructures and bioSystems at Surfaces" (S^3), INFM-CNR, 41100 Modena, Italy*
[2]*Dipartimento di Fisica, Università di Modena e Reggio Emilia, 41100 Modena, Italy*
[3]*Department of Chemistry, University of Manchester, M13 9PL Manchester, United Kingdom*
[4]*School of Chemistry, University of Edinburgh, EH9 3JJ Edinburgh, United Kingdom*

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We report on the Fe_{17} high-spin molecular cluster and show that this system is an exemplification of nanostructured dipolar magnetism. Each Fe_{17} molecule, with spin $S = 35/2$ and axial anisotropy as small as $D \simeq -0.02$ K, is the magnetic unit that can be chemically arranged in different packing crystals while preserving both the spin ground state and anisotropy. For every configuration, molecular spins are correlated only by dipolar interactions. The ensuing interplay between dipolar energy and anisotropy gives rise to macroscopic behaviors ranging from superparamagnetism to long-range magnetic order at temperatures below 1 K.

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A rejuvenated interest in phase transitions driven only by dipolar interactions has emerged since the experimental discovery that the magnetic molecular materials Cr_4 [1] and Mn_6 [2,3] provide attractive examples of pure dipolar magnets. These are nanostructured such that molecular clusters replace what atoms are to conventional materials. Quantum-mechanical superexchange interactions within each molecule result in net (high-)spin values per molecule at low temperatures. In parallel, dipolar interactions provide the only source of coupling between the molecular spins arranged in crystallographic lattices. Assuming each molecule as a high-spin pointlike dipole, the macroscopic properties of dipolar magnets can be precisely predicted because dipole-dipole interactions are calculated without involving any adjustable parameter [3–8]. These ideal materials are, however, very difficult to obtain. As often is the case, intermolecular superexchange interactions may not be negligible at very low temperatures where long-range magnetic order (LRMO) takes place. The consequence is that correlations between the molecules are often established by quantum-mechanical superexchange interactions at short ranges, whose macroscopic prediction is made difficult by their strong dependence on electronic details. Indeed, intermolecular superexchange interactions were found to be responsible for the observed LRMO in the high-spin molecular clusters Fe_{19} [9], Mn_4Br [10], Mn_4Me [11], and Fe_{14} [12], while they likely play a major role also in Mn_{12}-ac [13].

The absence of any superexchange pathway between the molecules is not the only prerequisite needed for the experimental observation of dipolar order. An obvious requirement is that molecules should have large molecular spins to lead to accessible ordering temperatures. Another complication is added by the cluster magnetic anisotropy. Crystal-field effects give rise to anisotropy energy barriers for each molecule that result in slow magnetic relaxation below a certain blocking temperature. The cluster anisotropy energies favor the molecular spin alignment along dictated directions, thus competing with the intermolecular coupling. The anisotropy, therefore, has to be very small, such that the spin-lattice relaxation is kept sufficiently fast down to temperatures low enough for LRMO to be observed [2,11].

In this Letter, we present the Fe_{17} molecular nanomagnet [14], containing 17 Fe^{3+} atoms per molecule linked via oxygen atoms (Fig. 1). Carrying very-large spin $S = 35/2$ and axial anisotropy as small as $D \simeq -0.02$ K, the Fe_{17} high-spin molecular cluster represents an excellent candidate for these studies. In addition, these molecules are bound together in the crystal only by van der Waals forces, thus prohibiting any intermolecular superexchange pathway. What makes Fe_{17} a *unique* model system is that we are able, by changing the crystallization conditions, to change the molecular packing *without* affecting the individual molecules, that is, keeping the surrounding ligands, the molecular high-spin ground state, and magnetic anisotropy unaltered. In other words, we succeed for the first time

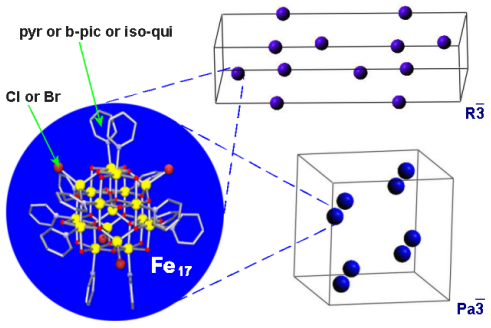

FIG. 1 (color online). The Fe_{17} molecule containing 17 magnetically coupled Fe^{3+} atoms (brighter, darker, and smaller balls represent Fe, Br or Cr, and O atoms, respectively), together with the packing in two different unit cells: $R\bar{3}$ (trigonal) and $Pa\bar{3}$ (cubic) [16].

in efficiently tuning the dipolar coupling between molecules with respect to the single-molecule properties. The resulting interplay gives rise to macroscopic behaviors ranging from superparamagnetic blocking to LRMO.

The Fe_{17} molecules are obtained by dissolving either $FeBr_3$ or $FeCl_3$ in a coordinating base, e.g., pyridine (pyr), beta-picoline (b-pic), or isoquinoline (isoqui) that also acts as solvent. To crystallize the product (Fe_{17}), we slowly diffuse a second (often noncoordinating) cosolvent such as diethyl-ether (Et_2O), acetone (Me_2CO), acetonitrile (MeCN), isopropylalcohol (IPA), etc., into the basic solution. The product is generally soluble in the first solvent (e.g., pyr) but insoluble in the second (e.g., Et_2O), and, by slowly diffusing the second solvent in, we crystallize the product. In this way, we obtain several derivatives having the same Fe_{17} magnetic core [15]. While the spin value is preserved throughout the whole Fe_{17} family, the anisotropy may change significantly. We have synthesized a number of new Fe_{17} clusters containing bromide ions in which we can either (i) exchange the pyr ligands for b-pic or isoqui ligands (Fig. 1), thus modifying only the outer organic coating of the Fe_{17}, such that the major change is purely intramolecular (*anisotropy*), or (ii) change the crystallizing cosolvent such that we change only the packing (*space group*) of the molecules in the crystal. For example, the reaction between $FeBr_3$ and pyr in the presence of Me_2CO affords the Fe_{17} magnetic core crystallized in the trigonal space group $R\bar{3}$, while the same reaction but in the presence of IPA gives an identical Fe_{17} magnetic core but crystallized in the cubic space group $Pa\bar{3}$ (Fig. 1). By defining the organic ligand and subsequent crystallizing conditions, we can therefore reproducibly generate different arrays of this molecular magnet. In what follows, we focus on the above-mentioned Br derivatives of the Fe_{17} molecule having trigonal or cubic symmetries [16]. Measurements of magnetization down to 2 K and specific heat down to ≈ 0.3 K on powder samples were carried out for the $0 < H < 7$ T magnetic field range. Magnetization, susceptibility and relaxation measurements below 2 K were performed using homemade Hall microprobes. In this case, the grainlike samples consisted of collections of small crystallites of ca. 10^{-3} mm^3. For measurements performed on powder samples, the calculated fits were obtained taking into account spin random orientations.

Field dependencies of the molar magnetization $M(H)$ for both Fe_{17}-trigonal and Fe_{17}-cubic were collected for $T = 2$, 5, and 20 K (Fig. 2). The important result is that the $M(H)$ curves depend on the applied field in an *identical* manner regardless of the trigonal or cubic symmetry. This implies that the Fe_{17} magnetic molecule (that is, the spin ground state and anisotropy) is the same in both complexes. If we consider the single-spin Hamiltonian $\mathcal{H} = DS_z^2 + g\mu_B\vec{H}\cdot\vec{S}$, the magnetization in the whole field range can be well fitted with net molecular spin $S = 35/2$, zero-field splitting $D = -0.023$ K, and $g = 2.06$ for both complexes. Although smaller trigonal components could be present, the data do not justify a more sophisticated fitting.

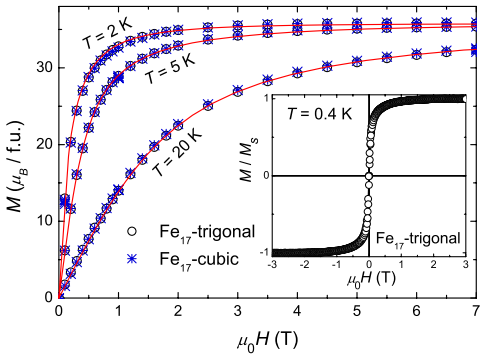

FIG. 2 (color online). Isothermal molecular magnetization for both Fe_{17}-trigonal (○) and Fe_{17}-cubic (*) collected at $T = 2$, 5, and 20 K. Solid lines are the results of the fit (see text), yielding net molecular spin $S = 35/2$ and axial $D = -0.023$ K. Inset: Hysteresis loop of Fe_{17}-trigonal at $T = 0.4$ K.

Figure 3 shows the collected specific heat $C(T, H)$ data of both Fe_{17} molecular compounds as a function of temperature for several applied fields. At first sight and as for the $M(H)$ data (Fig. 2), the $C(T, H)$ of the Fe_{17}-trigonal does not differ from that of the Fe_{17}-cubic, at least for $H > 0$. The main difference is in the zero-applied-field data for which a λ-type anomaly centered at $T_C = 0.81$ K is observed for trigonal symmetry (inset in Fig. 3). Anticipating the discussion below, this feature reveals the onset of LRMO; the magnetic nature is indeed proven by its disappearance upon application of H. Clearly, the λ-type anomaly arises on top of a much broader one, which shifts with increasing applied field towards higher temperatures. Because of the small anisotropy ($D \simeq -0.02$ K), it is expected that the magnetic contribution to $C(T, H)$ for $H \geq 1$ T is due to Schottky-like Zeeman splitting of the otherwise nearly degenerate energy spin states. Indeed, the calculated Schottky curves (solid lines in Fig. 3) arising from the field-split levels account very well for the experimental data. The same behavior is followed by Fe_{17}-cubic except that no sign of LRMO is apparently observed.

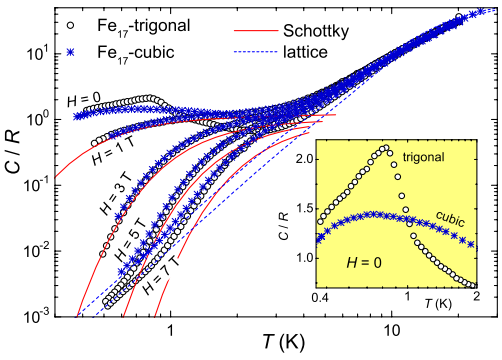

FIG. 3 (color online). Specific heat of Fe_{17}-trigonal and Fe_{17}-cubic for several applied fields, as labeled. Drawn curves are explained in the text. Inset: Magnification of the low-T/zero-field range showing the different ordering behaviors.

As particularly evident in the low-T/high-H region in Fig. 3, phonon modes of the crystal lattice contribute differently to $C(T)$ of Fe_{17}-trigonal and Fe_{17}-cubic. We estimated the lattice contributions (dashed lines in Fig. 3) by fitting to a model given by the sum of a Debye term for the acoustic low-energy phonon modes plus an Einstein term that likely arises from intramolecular vibration modes. From the field dependencies of $M(T, H)$ and $C(T, H)$, we have already deduced that the individual Fe_{17} molecule remains identical regardless of space group. Therefore, it is not surprising that the fit provides the same Einstein temperature $\theta_E \simeq 42$ K for both compounds (Fig. 3). Contrary, low-energy phonon modes result in different Debye temperatures whose values are $\theta_D \simeq 23$ and 28 K for Fe_{17}-cubic and Fe_{17}-trigonal, respectively. Because Fe_{17}-cubic has larger intermolecular distances [16], softer low-energy modes, yielding smaller θ_D, are indeed to be expected. The so-obtained lattice contributions allow us to estimate the entropy changes ΔS by using the relation $\Delta S/R = \int_0^\infty C_m(T)/(RT)dT$, where $C_m(T)$ is the magnetic contribution obtained from $C(T)$ after subtraction of the respective lattice contribution. For both compounds, the obtained ΔS amounts to $3.7R$, which is in good agreement with the entropy expected $R\ln(2S + 1) \simeq 3.6R$, given $S = 35/2$. As already anticipated, we can therefore safely attribute $T_C = 0.81$ K to the LRMO temperature of the molecular spins in Fe_{17}-trigonal.

Susceptibility measurements (Fig. 4) reveal sharp anomalies that take place at $\sim T_C$ for Fe_{17}-trigonal, corroborating the LRMO deduced from specific heat data and at $T_B \simeq 0.5$ K for Fe_{17}-cubic, whose nature is discussed below. For $T > 4$ K, both susceptibilities tend to overlap each other (Fig. 4). The observed behavior in Fe_{17}-trigonal is compatible with a ferromagnetically ordered phase, in which demagnetization effects become important. The measured susceptibility at T_C is close to the estimated limit for a ferromagnetic grainlike sample, $\chi_N = 1/\rho N \simeq 227$ emu/mol (see Fig. 4), where $\rho = 3.32$ g/cm^3 is the density of Fe_{17}-trigonal, and $N = 4\pi/3$ is the demagnetizing factor of the grainlike sample, approximated to a sphere. For the 5 K $\lesssim T \lesssim$ 80 K temperature range, the fit to the Curie-Weiss law $\chi = C/(T - \theta)$ for the susceptibility of Fe_{17}-trigonal corrected for the demagnetizing field, $\chi = \chi'/(1 - \rho N\chi')$, provides $C = 175.4$ emu K/mol and $\theta = 0.9$ K, in agreement with the observed ferromagnetic order at $T_C \simeq 0.8$ K. The Curie constant C equals (within error) the expected value of a (super)paramagnet with spin $S = 35/2$ and $g = 2.06$, as deduced above from the magnetization data. This analysis is corroborated by the hysteresis loop we collected in the ordered phase (inset in Fig. 2), for which Fe_{17}-trigonal behaves as a soft ferromagnet with a coercivity of $\sim$60 Oe. We recall that from $M(H)$ curves, we estimated the anisotropy $D = -0.023$ K, which likely causes a pinning of the domain-wall motions responsible therefore for the slow decrease of the experimental susceptibility below T_C (Fig. 4).

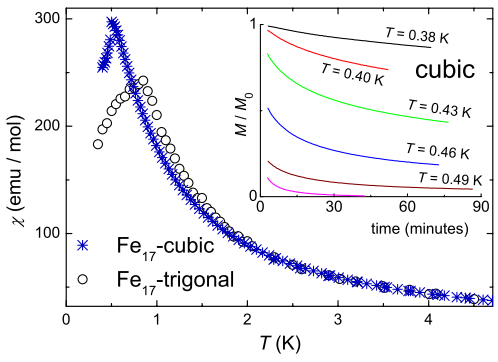

FIG. 4 (color online). Magnetic susceptibility of Fe_{17}-trigonal and Fe_{17}-cubic for $H = 0.01$ T. Inset: Time decay of M for Fe_{17}-cubic, measured at zero-applied field after saturation for the indicated temperatures.

The occurrence of a sharp peak at $T_B \simeq 0.5$ K in the susceptibility of Fe_{17}-cubic (Fig. 4) has apparently no counterpart in the specific heat (inset in Fig. 3). We therefore exclude LRMO as a possible source. We recall that intermolecular distances for Fe_{17}-cubic are slightly larger than that of Fe_{17}-trigonal [16]. It is then reasonable to assume that in Fe_{17}-cubic the intermolecular coupling is weaker and that the molecular anisotropy is the predominant energy. This would lead to superparamagnetic blocking at T_B of the molecular spins along preferred directions dictated by the anisotropy. To better elucidate this point, we performed magnetic relaxation experiments in Fe_{17}-cubic at temperatures below T_B. We first applied a field necessary to saturate the magnetization of the sample at 2 K. We then cooled down to a given temperature below T_B, and, upon removing the field, we followed the relaxation of the Fe_{17} molecules to thermal equilibrium by collecting the time decay of the magnetization. Results are shown in the inset in Fig. 4, where it is seen that the decay neatly slows down below T_B, as expected for a superparamagnet. Magnetization data are well described by a stretched exponential decay $M/M_0 = \exp(-t/\tau)^\beta$, where M_0 is the initial magnetization, β the stretched parameter, and τ the characteristic decay time. The T dependence of τ (not presented here) follows an Arrhenius law providing the activation energy $U = 9.0$ K that, given $S = 35/2$ and $U = -D(S^2 - 1/4)$, corresponds to $D \simeq -0.03$ K, which is of the same order of that estimated above. We note that U of the Fe_{17} molecule is about 8 times smaller than that of the well-known single-molecule magnet Mn_{12}-ac [17]. As a result of similar spin dynamics, the same ratio holds for the respective blocking temperatures as well.

The Fe_{17} molecules are magnetically isolated from each other as evidenced by the large intermolecular distances; for instance, *all* Fe-Fe distances are greater than 8.7 Å for adjacent molecules in Fe_{17}-trigonal. A close inspection of the crystallography of both materials does not reveal any intermolecular superexchange pathway nor any evidence of π stacking of the pyridine rings [16]. These facts show that the dipolar interaction is solely responsible for the observed macroscopic behaviors. By switching from trigo-

nal to cubic symmetry, we change not only the arrangement and reciprocal distances of the Fe_{17} molecules but, accordingly, also the dipolar interaction energies E_{dip}. We performed extensive calculations of E_{dip} assuming several magnetic configurations of $S = 35/2$ pointlike dipoles arranged in analogous crystallographic lattices to that of Fe_{17}-trigonal and Fe_{17}-cubic. In particular, the position of the spins was fixed accordingly to molecular centroids. Interestingly, for E_{dip} we found up to an order of magnitude change by switching from cubic to trigonal symmetry. Since the distance between nearest neighbors changes by less than 10% by switching from Fe_{17}-cubic to Fe_{17}-trigonal [17], one has to conclude that lattice symmetries play the major role in determining E_{dip}. This neatly illustrates that the nature of the magnetic order should not be deduced by simply comparing the ordering temperature with the interaction energy between a pair of nearest spins.

For Fe_{17}-trigonal, the magnitude of the calculated E_{dip} does justify that LRMO is here driven by dipolar coupling between the molecules. We do not have, however, enough evidence to discriminate which magnetic structure is realistically the most probable one. Among the magnetic structures considered in our simulations and on the basis of our experimental data suggesting a ferromagnetic nature of the ordered phase, promising candidates seem to be the alignment of the molecular spins along the [100] direction and that along the $[2\bar{2}1]$ direction. These configurations have indeed the lowest calculated values ($-E_{dip} \simeq 0.8$ and 0.6 K, respectively), which are of the correct order with respect to the experimental $k_B T_C$. We here anticipate that preliminary neutron diffraction experiments [18] have recently corroborated the onset of the magnetic phase transition for Fe_{17}-trigonal.

In summary, we have developed a synthetic strategy to prepare (Fe_{17}) nanomagnets with varying crystal symmetry. We experimentally demonstrate that Fe_{17} represents the first molecular system to undergo either LRMO or superparamagnetic blocking of the molecular spins depending on the symmetry. We show that this results from the interplay of the dipolar magnetic coupling between the molecular spins, with respect to the single-molecule magnetic anisotropy. That supramolecular chemistry leads to fascinating ordered arrangements of identical high-spin nanomagnets is no novelty; that these arrangements can be achieved without affecting the magnetic properties of the individual nanomagnets (e.g., keeping unaltered the cluster spin ground state and magnetic anisotropy) is a step forward in the manipulation of the magnetic interactions at the nanometer scale. The Fe_{17} system is, therefore, a test model material for workers interested in the modelization of phase transitions purely driven by dipolar interactions.

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*To whom all correspondence should be addressed. Electronic address: evange@unimore.it

[1] A. Bino *et al.*, Science **241**, 1479 (1988).
[2] A. Morello *et al.*, Phys. Rev. Lett. **90**, 017206 (2003).
[3] A. Morello *et al.*, Phys. Rev. B **73**, 134406 (2006).
[4] P. Panissod and M. Drillon, in *Magnetism: Molecules to Materials IV*, edited by J. S. Miller and M. Drillon (Wiley-VCH, Weinheim, Germany, 2002), Chap. 7.
[5] J. F. Fernández and J. J. Alonso, Phys. Rev. B **62**, 53 (2000); **65**, 189901(E) (2002); **73**, 024412 (2006).
[6] J. F. Fernández, Phys. Rev. B **66**, 064423 (2002).
[7] X. Martínez-Hidalgo, E. M. Chudnovsky, and A. Aharony, Europhys. Lett. **55**, 273 (2001).
[8] J. F. Fernández (unpublished); see also M. Evangelisti *et al.*, Phys. Rev. Lett. **95**, 227206 (2005).
[9] M. Affronte *et al.*, Phys. Rev. B **66**, 064408 (2002).
[10] A. Yamaguchi *et al.*, J. Phys. Soc. Jpn. **71**, 414 (2002).
[11] M. Evangelisti *et al.*, Phys. Rev. Lett. **93**, 117202 (2004).
[12] M. Evangelisti *et al.*, Appl. Phys. Lett. **87**, 072504 (2005).
[13] F. Luis *et al.*, Phys. Rev. Lett. **95**, 227202 (2005).
[14] G. W. Powell *et al.*, Angew. Chem., Int. Ed. **43**, 5772 (2004).
[15] For instance, the reaction between $FeCl_3$ and pyr in the presence of MeOH produces the complex $Hpyr[Fe_{17}O_{16}(OH)_{12}(pyr)_{12}Cl_4]Cl_4$ whose structure and preliminary magnetic properties were recently reported in Ref. [14], where we showed that it has $S = 35/2$ and small cluster anisotropy.
[16] The compound Fe_{17}-trigonal crystallizes in space group $R\bar{3}$ with $a = b = 16.2552(6)$ Å, $c = 71.919(5)$ Å, whereas Fe_{17}-cubic crystallizes in space group $Pa\bar{3}$ with $a = b = c = 29.2854(3)$ Å. From the unit cell volumes, we obtain the mean values of the intermolecular separations (assumed as the centroid to centroid distances): 13.9 Å for Fe_{17}-trigonal and the slightly larger value of 14.6 Å for Fe_{17}-cubic. CCDC-612322 and CCDC-612323 contain the supplementary crystallographic data for Fe_{17}-cubic and Fe_{17}-trigonal, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, United Kingdom; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk].
[17] R. Sessoli *et al.*, Nature (London) **365**, 141 (1993).
[18] Rutherford Appleton Laboratory, experimental report No. RB510053, Instr. GEM, ISIS, 2005; Canadian Neutron Beam Centre, experimental report No. CNBC-615, Instr. C2, 2006.